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Deterioration of natural hydraulic lime mortars, II: Effects of chemically accelerated leaching on physical and mechanical properties of carbonated materials

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ABSTRACT

Masonry using lime binders is very common in all regions of the world. Models for the future climate in northern regions predict conditions conducive for the materials used in mass masonry being saturated for longer periods and therefore at higher risk of binder leaching and consequent deterioration. Following work on uncarbonated lime mortars, ammonium nitrate leachant was used to accelerate the deterioration of carbonated mortars containing natural hydraulic lime binders. Leaching of binder significantly reduced the strength of the mortar and slightly increased its sorptivity. The resistance to deterioration increased in the order NHL2<NHL3.5<NHL5 binder, in line with the increasing hydraulicity of the binder. Carbonated mortars are more resistant to binder leaching than the corresponding uncarbonated materials.

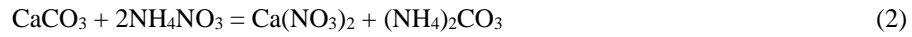
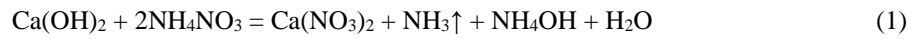
Keywords: natural hydraulic lime, mortar, binder, dissolution, leaching

1 INTRODUCTION

Traditional stone masonry, in the form of units bedded in lime mortar, is common worldwide. As a component of the external envelope of a building it must contribute to resisting the environment. There are three possible ways in which the interaction of water from the environment with masonry could change in response to climate change. First, in temperate northern zones the predicted increases in rainfall [1,2] suggest that masonry will remain wetter for longer, as a result both of wind-driven rain and of increased penetration into exposed infrastructural masonry (bridge piers, etc). Second, where there is no damp-proof course at the base of a wall, evaporation from wall surfaces draws moisture from the ground and has the potential to drive significant amounts of water through the bed joints of masonry. Higher temperatures will increase the severity of this so-called evaporative pumping [3,4]. Third, the reduction of CO₂ emissions to mitigate climate change encourages retrofitting of thermal insulation to masonry buildings and this is likely to change the kinetics of moisture flow through masonry walls and potentially lead to build-up of moisture, especially if the insulation is of low water vapour permeability [5,6]. These higher moisture contents and water flows have the potential to leach binder from the mortar. In this process soluble components within the mortar dissolve and migrate to be re-deposited within pores, in construction voids or on the external face of masonry. This loss of binder has been reported by building professionals, with voids found in walls behind an apparently sound exterior [7,8], and is associated with progressive collapse in traditional buildings [9]. The first part of this study [10] reported, for the first time, the kinetics of lime binder leaching in uncarbonated natural hydraulic lime (NHL) mortars (such as those in the core of existing mass masonry or those in newly built work before atmospheric exposure has caused carbonation) and proposed a simple predictive model. This complementary paper aims to establish the rate of soluble binder leaching from carbonated natural hydraulic lime mortars (such as those expected to be near the surface and exposed to atmospheric CO₂) and its effect on properties and performance. The objectives were to determine the rate of calcium leaching in a range of carbonated NHL mortars, using ammonium nitrate as an accelerated leachant, and to assess the effect on strength and moisture handling characteristics. This would inform a method for predicting the service life of lime mortar.

Forster et al [10] note that the lime binder components vulnerable to dissolution are portlandite (calcium hydroxide, Ca(OH)₂) and calcite (calcium carbonate, CaCO₃). The hydraulicity of the original binder influences a mortar's long term performance: less hydraulic limes have more Ca(OH)₂ and less

of the hydraulic calcium silicate minerals and are therefore more reliant on carbonation for hardening, whilst more hydraulic limes have less Ca(OH)_2 and more calcium silicate. Consequently less hydraulic lime binders should be more susceptible to dissolution. This will also be aggravated in saturated, cold conditions because the solubility of both Ca(OH)_2 and CaCO_3 increases as water temperature decreases [11]. Accelerated leaching has been successfully used in cement and concrete studies [12,13] and Forster et al [10] refined the method for lime binder to reflect its different composition and solubility, confirming that the loss of calcium from the hardened products changes the properties and performance of the uncarbonated mortar. The principle of chemical leaching is to promote reaction between calcium hydroxide or carbonate (in the binder material) and ammonium nitrate in the leachant solution, forming species that are highly soluble in water (see equations 1 and 2).

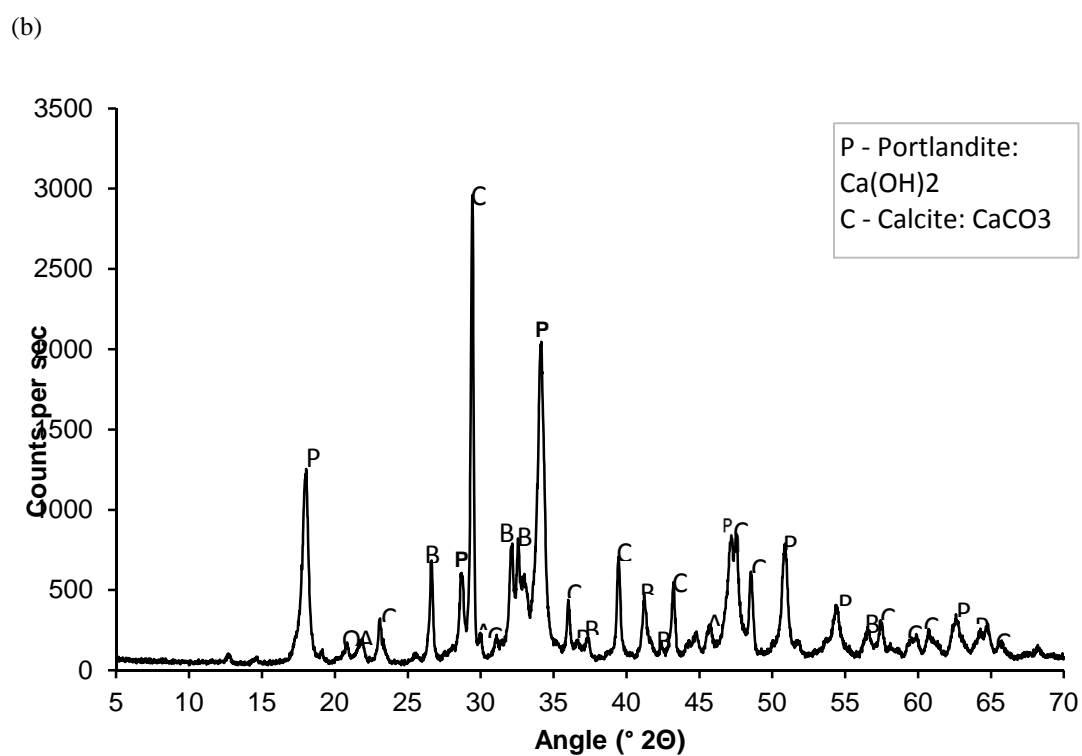
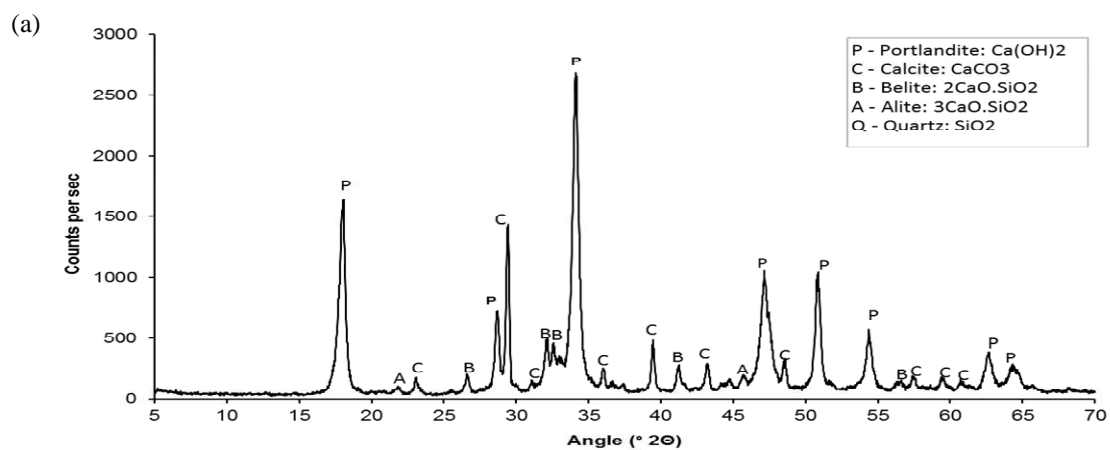


Because the leachant concentration used in cement leaching proved too aggressive for NHL specimens, 1 M ammonium nitrate solution was used in both parts of this work [10, this paper] to accelerate the leaching of calcium (Ca^{2+}) ions.

2 MATERIALS, SPECIMEN MANUFACTURE AND CURING

2.1 Materials and characterisation

Mortars were prepared at a constant binder to aggregate ratio of 1:3 (by volume) using well graded siliceous sand (Cloddach concrete sand, Elgin, Scotland). Using this sand ensured that binder leaching is not confused with dissolution of calcareous components from the aggregate. The particle size distribution was determined by sieving in accordance with BS EN 13139 [14], as previously reported [10]. The bulk density of the aggregate is 1500 kg/m^3 . St Astier NHL2, NHL3.5 and NHL5, of bulk densities 550, 620 and 750 kg/m^3 respectively and complying with BS EN 459-1: 2010 [15], were used. The mineral compositions (X-Ray diffractograms, Figures 1a-c) and manufacturer's anhydrous binder composition (Table 1) were the same as in part 1 of this work [10]. In these limes the amount of Ca(OH)_2 decreases as the hydraulicity of the material increases and this influences the potential for leaching [11].



(c)

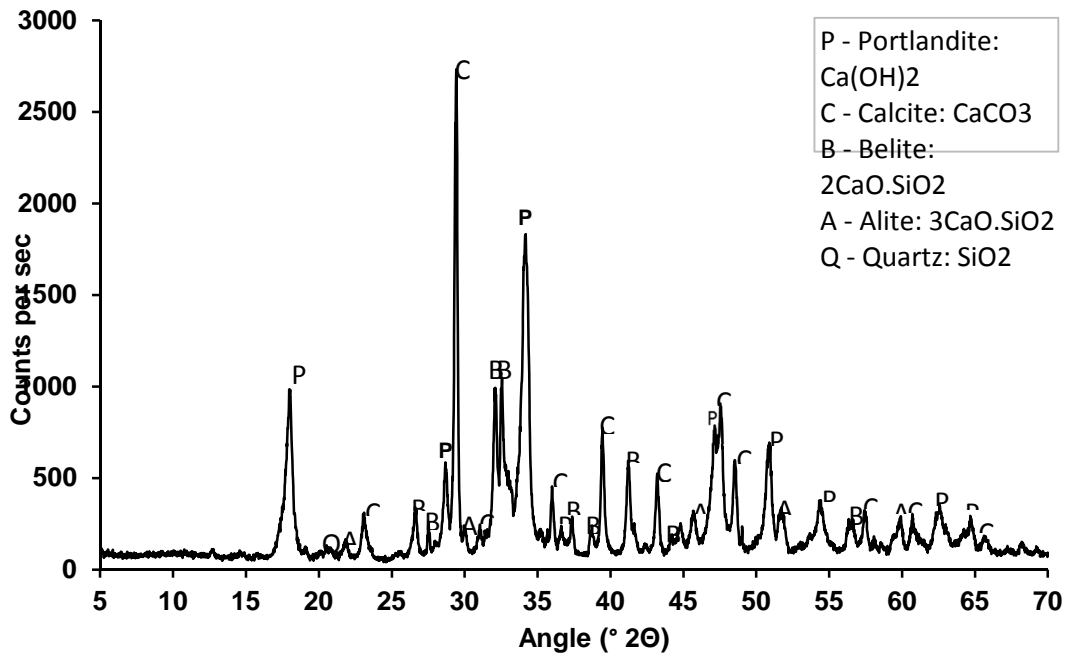


Figure 1: X Ray diffractograms for anhydrous Natural Hydraulic Lime (NHL) binders. (a) NHL2, (b) NHL3.5, (c) NHL5

Table 1: Chemical and physical properties of the NHL binders (source: manufacturer)

Binder	Bulk density kg/m ³	Mineralogical composition (%)							
		CaCO ₃ unburnt	Insoluble	Free Ca(OH) ₂	Compound				
					C ₂ S	C ₃ A	C ₂ AS	C ₄ AF	CaSO ₄
NHL2	550	13	8	58	17	0.4	0.8	0.4	0.5
NHL3.5	620	25	9.6	25	35	0.5	1	0.5	0.8
NHL5	750	23	5.6	22	43	0.7	1.3	0.7	0.7

2.2 Mortar manufacture and batching

The mixing procedure for the manufacture of mortar test specimens was closely aligned to BS EN 459-2 [16] and BS EN 1015-2 [17] for the testing of lime mortars. The standards refer to the mixing procedure stipulated in BS EN 196-1 [18] for the testing of cements. Whilst BS EN 196-1 specifies a 1:3 ratio (1350g of aggregate to 450g of binder) with 225g of de-ionised water, BS EN 459-2 varies the water content to ensure the mortar achieves a flow of 165±2mm for NHL2 and NHL 3.5 and a flow of

185mm \pm 2mm for NHL5 using a standard (BS EN 459-2) flow table apparatus [16]. In this programme, the proportions were further modified to integrate the relative bulk density for the different binder types to ensure a constant 1:3 ratio by volume was maintained for all mortars (Table 2).

The mixing and casting of the mortars followed BS 459-2 (2010) [16], except that 160x40x40mm lightweight polystyrene moulds were used in place of the specified steel gang moulds, in order to reduce the load on the shelving in the environmental curing cabinet. The polystyrene gang moulds were not treated with releasing agent to avoid possible adverse effects on the mould material or the mortar. Table 2 shows the quantities required for 8 litres (0.008 m³) of mortar. Fifteen 160x40x40 mm prisms were produced for each binder and carbonated before leaching, of which three were used as controls.

Table 2: Mortar mix data

Lime	Mass of material kg			Sand/lime by mass	Water/lime by mass	Flow value mm (\pm 2mm)
	NHL	Sand	Water			
NHL 2	1.63	7.50	2.63	4.6	1.61	165
NHL3.5	1.89	7.50	2.73	4.0	1.44	165
NHL 5	2.05	7.50	2.75	3.7	1.34	185

2.3 Curing and carbonation regime

The specimens were cured in a TAS series 3 environmental cabinet at 100% RH and 20°C for 6 days, after which they were de-moulded and the RH level in the cabinet was reduced to 65% (+/- 5%). This lower humidity promotes the carbonation reaction and, according to Lawrence [19], the specimens are expected to be dry enough for carbonation to start by 14 days. An injection system maintained a constant CO₂ level of 800-1000ppm to accelerate the carbonation process to achieve the target depth of 20mm (marking full carbonation of the 40 x 40 mm prisms) by the end of 56 days, and the total curing and carbonation time chosen to be in line with Pavia and Toomey [20] and to accord with part 1 [10].

3 EXPERIMENTAL PROCEDURE

3.1 Accelerated leaching

The leaching procedure was the same as described in part 1 of this work [10]. After 56 days of curing, specimens contained in individual wire cages (1M ammonium nitrate experiments) or placed on glass spacers (deionised water experiments) were immersed for up to 169 days at $20\pm 2^{\circ}\text{C}$ in a stirred tank. The control specimens were immersed in de-ionised water in parallel treatments for the initial 36 days. In each case up to 20 specimens were exposed to 15L of leachant.

3.2 Physical and chemical testing

Specimens were removed from solution after 1, 4, 9, 16, 25, 36, 100 and 169 days and tested as follows. Unfortunately, insufficient specimens were available to complete all tests at 100 and 169 days, and it was necessary to curtail the water leaching after 36 days, as noted below.

3.2.1 Flexural Strength

Flexural strength was tested according to BS EN 459-2 [16] using three point bending in a Lloyds universal MK5 instrument of 5kN maximum load capacity. Force was increased until failure occurred and the specimen broke in two. The two halves were preserved for other tests.

3.2.2 Depth of carbonation

The fractured surfaces were sprayed with 1.0% phenolphthalein solution to give an indication of the penetration of the carbonation front as a result of the curing and accelerated carbonation process.

3.2.3 Sorptivity

The specimens were oven dried at 85°C for 24 hours and then their sorptivity determined [3,10]. Each specimen was allowed to cool and then five faces were coated with resin, leaving the 40 x 40 mm fracture surface uncoated. Each specimen was supported on a pair of glass rods located in the bottom of a container and the uncoated face immersed to a depth of 1mm in de-ionised water. Measurements of mass increase were taken at intervals over about one hour. The sorptivity determined from the slope of the straight line relationship between mass and $t^{1/2}$, is expressed in units of $\text{mm}/\text{min}^{1/2}$ [3]. It may be noted that sorptivity is equivalent, in principle, to the water absorption coefficient, determined

according to BS EN ISO 15148 [21]. A sorptivity of $1 \text{ mm/min}^{1/2}$ is equal to a water absorption coefficient of $0.13 \text{ kg/m}^2\text{sec}^{1/2}$.

3.2.4 Compressive testing

Compressive strength was tested in accordance with BS EN 459-2 [16] using the remaining half of each prism. The fractured half was trimmed with a diamond saw (dry blade) to produce a 40mm cube which was then tested in the Lloyds universal MK5 testing machine.

3.2.5 Petrographic analysis

Thin sections, prepared and impregnated with blue dyed resin to highlight porosity, were investigated by petrographic microscopy and a quantitative assessment to identify binder, aggregate and porosity undertaken by the point counting method previously described [10].

4 RESULTS

Physical testing results for all carbonated specimens subjected to ammonium nitrate and water leaching are presented here.

4.1 Degree of carbonation

The absence of pink coloration on the fractured surfaces when sprayed with phenolphthalein solution confirmed that the procedure described in section 2.3 resulted in fully carbonated specimens at the start of the leaching treatment although it is possible that there may be a small amount of residual Ca(OH)_2 . Recognising that the proportion of free Ca(OH)_2 in the NHL binders varies [10] and carbonation converts the Ca(OH)_2 to CaCO_3 , the resulting CaCO_3 content in the mortars decreases in the order $\text{NHL2} > \text{NHL3.5} > \text{NHL5}$.

4.2 Compressive and flexural strength results

Table 3 shows that there is a clear difference between the specimens leached in ammonium nitrate and in de-ionised water. In water, carbonated specimens of NHL2, i.e. samples that have a high proportion of CaCO_3 , lost strength, whilst those of NHL5, with more reliance on hydraulic set, gained strength

over the test period. This is probably associated with the favourable curing environment for the development of the products of hydration, especially C-S-H.

Table 3: Compressive, flexural strength and sorptivity results (each entry denotes a single test on a single specimen)

Binder	Leachant	Compressive strength MPa				Flexural strength MPa				Sorptivity mm/min ^½		Change in sorptivity %
		0 d	36 d	100 d	169 d	0 d	36 d	100 d	169 d	0 d	36 d	
NHL2	water	1.14	0.94			0.31	0			1.96	1.90	-3.1
NHL3.5	water	2.69	2.07			0.7	0.95			1.55	1.77	+14.2
NHL5	water	2.48	3.02			0.74	1.83			2.11	1.08	-48.8
NHL2	NH ₄ NO ₃	1.14	0.75	0.25	0.1	0.31	0.18	0.32	0.21	1.96	1.98	+1.0
NHL3.5	NH ₄ NO ₃	2.69	0.91	0.16	0.5	0.7	0.38	0.29	0.21	1.55	1.91	+23.2
NHL5	NH ₄ NO ₃	2.48	1.3	1.09	0.68	0.74	0.63	0.57	0.29	2.11	1.85	-12.3

In contrast, the effect of ammonium nitrate leaching on strength is significant, giving generally progressive reductions in compressive and flexural strength. Strength loss was more rapid with NHL2 than with the other binders and this is consistent with its higher proportion of CaCO₃ [10], which reacts according to equation (2) above.

4.3 Sorptivity

Due to lack of specimens, sorptivity data is available only for 0 and 36 days leaching. Table 3 shows that 36 days water and ammonium nitrate leaching has no effect on sorptivity of carbonated NHL2, increases sorptivity of carbonated NHL3.5 and decreases sorptivity of carbonated NHL5. This behaviour is not consistent with the strength reductions observed in NHL2 and NHL5 in both leachants. Possibly in NHL5 there is continuing hydration of C₂S during the leaching and the resulting formation of C-S-H fills the pores and counteracts any loss of CaCO₃. The significant increase in sorptivity observed in NHL3.5 could be because there is less C₂S and hence less C-S-H can form to offset the loss of CaCO₃.

4.4 Petrographic analysis

Figures 2-4 show the effect of 36 days ammonium nitrate leaching on mortars, viewed in thin section.

Blue is porosity, grey is aggregate and dark grey/brown is binder.

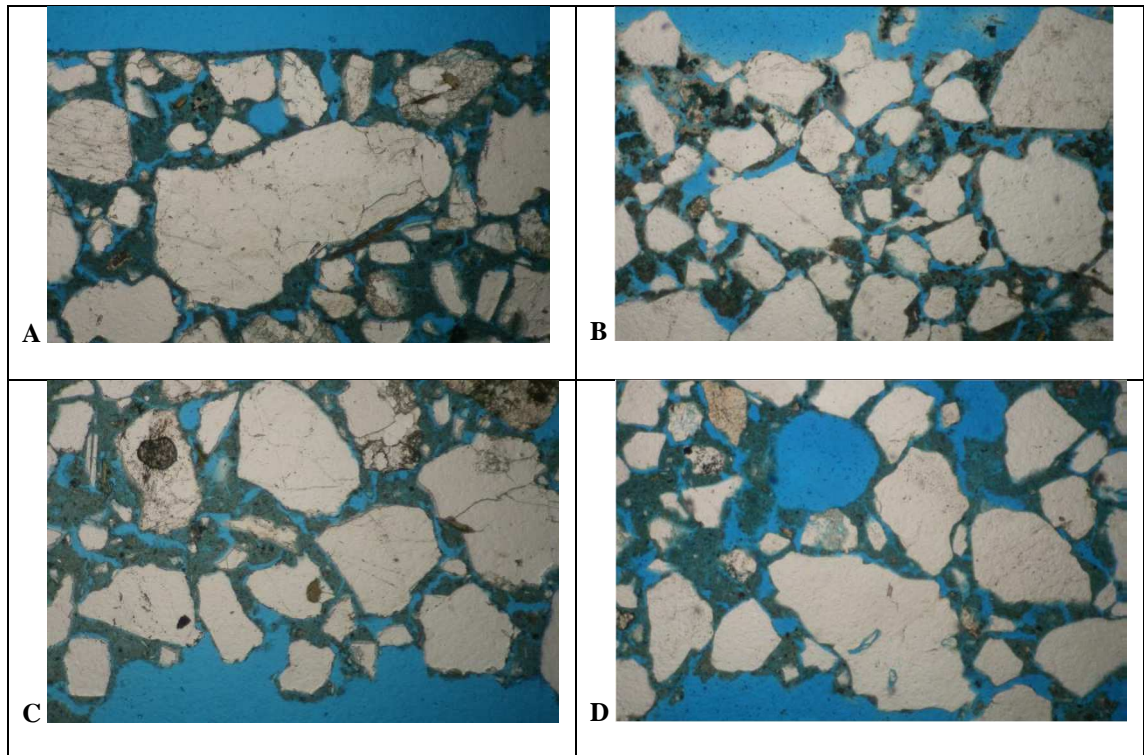


Figure 2: Carbonated NHL2 mortar thin sections: (A) Initial outer, (B) 36 days outer, (C) Initial inner, (D) 36 days inner.

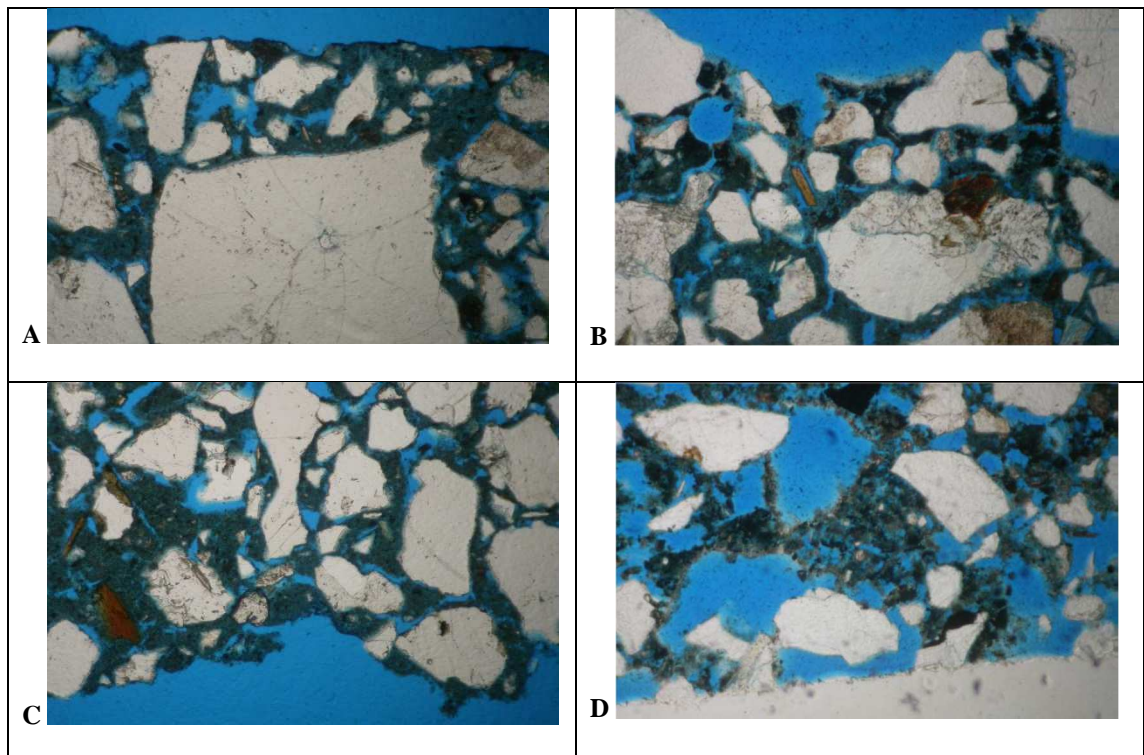


Figure 3: Carbonated NHL3.5 mortar thin sections: (A) Initial outer, (B) 36 days outer, (C) Initial inner, (D) 36 days inner.

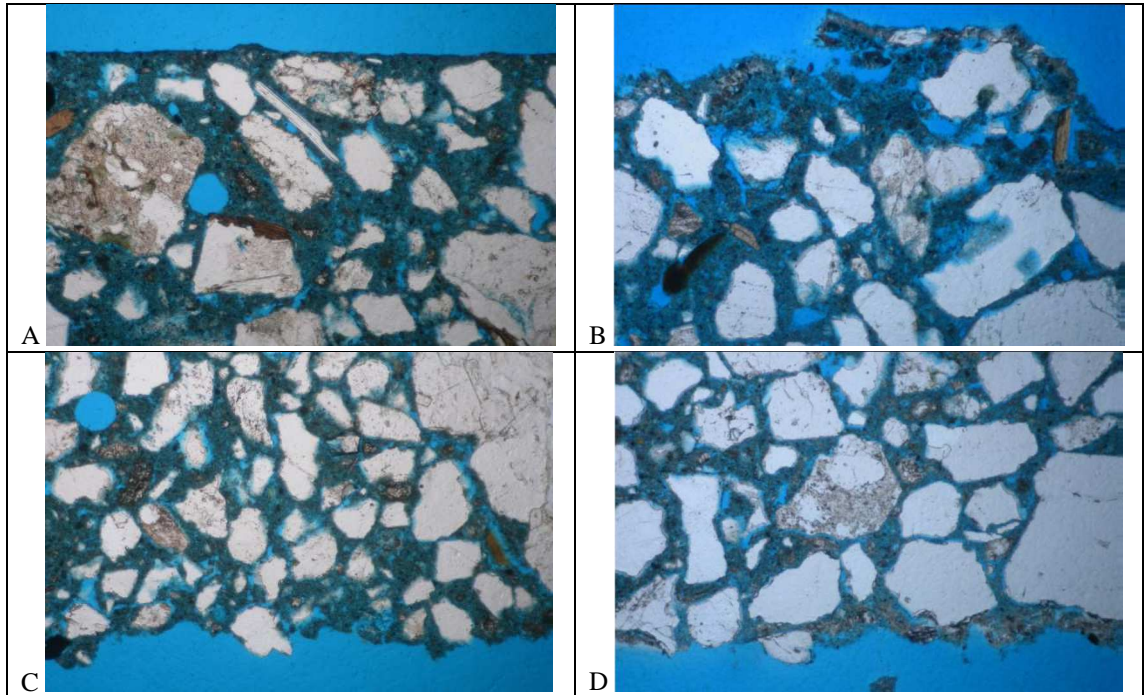


Figure 4: Carbonated NHL5 mortar thin sections: (A) Initial outer, (B) 36 days outer, (C) Initial inner, (D) 36 days inner.

The thin sections show features typical of carbonated NHL mortars. The aggregate is well graded and distributed and the bond (evaluated as the extent of contact between aggregate and binder) is good in NHL5 but less so in NHL2 and NHL3.5, with the latter in particular showing locally poor bonding. The bonding is slightly impaired towards the inner regions. Cracks increase in abundance and width towards the inner regions and are wider in the NHL2 and 3.5 mortars but smaller and better defined in the NHL5. This is because with the stronger binders, cracking during curing is more likely to occur at the weakest point (i.e. the aggregate-binder interface) whereas with the weaker binders cracking occurs preferentially within the binder. Carbonation is diffuse, with the typical crystalline components too small to be observed with the petrographic microscope. When the mortars are leached in ammonium nitrate, moderate binder depletion is evident throughout the NHL2 and 3.5 samples (Figures 2 and 3, images B and D) with widening of microcracks, minor loss of bond and enlargement of voids. In NHL3.5 there is complete loss of mortar integrity towards the inner region. NHL5 (Figure 4, images B

and D) shows only minor to moderate depletion with its overall integrity maintained but compromised at the outer surface. Compared to the uncarbonated mortars [10] the loss of binder is less significant in every case confirming that carbonated mortar is more resistant to leaching.

These trends are supported numerically by point counting analysis, which was done on different thin sections. This identifies the presence or absence of binder at each of 600 points across the section but does not take into account any changes in binder density and the results are conveniently presented in ternary diagrams [22]. As shown in Figure 5, leaching of binder would be expected to move the composition of a mortar parallel to the binder-porosity axis in the direction of higher porosity. Figure 5 also shows the location of the zone enlarged in Figures 6 and 7. Figure 6 shows the effect of 36 days leaching in ammonium nitrate on carbonated mortars. For comparison, Figure 7 shows the effect of 36 days leaching in ammonium nitrate on uncarbonated mortars, using the results presented in part 1[10].

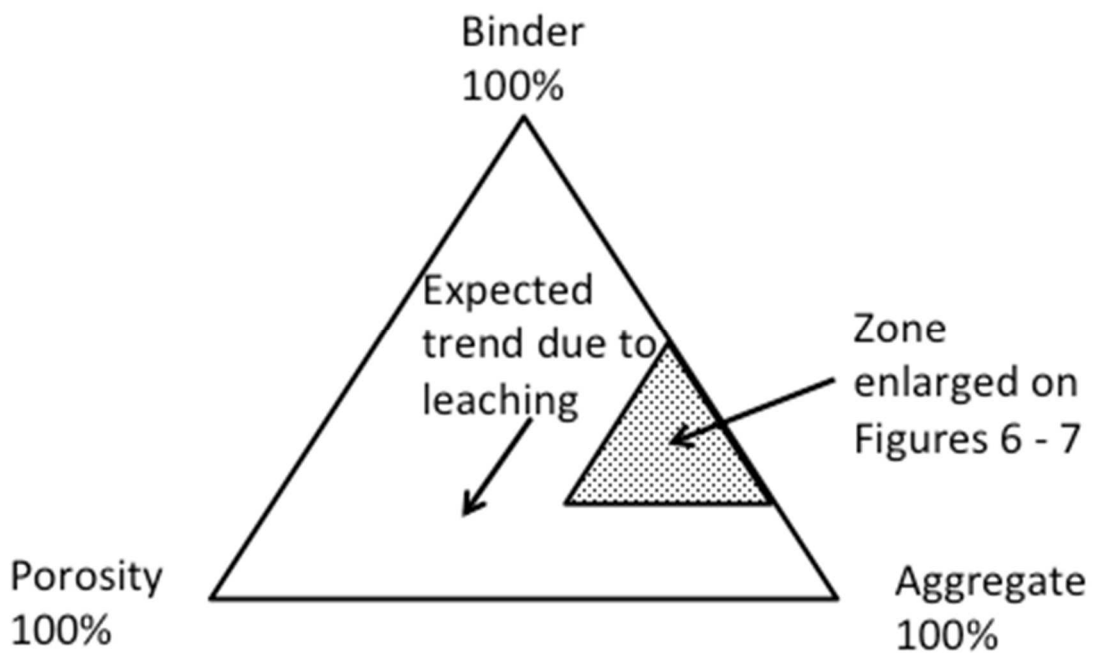


Figure 5: Schematic ternary diagram for mortar thin section point counting data

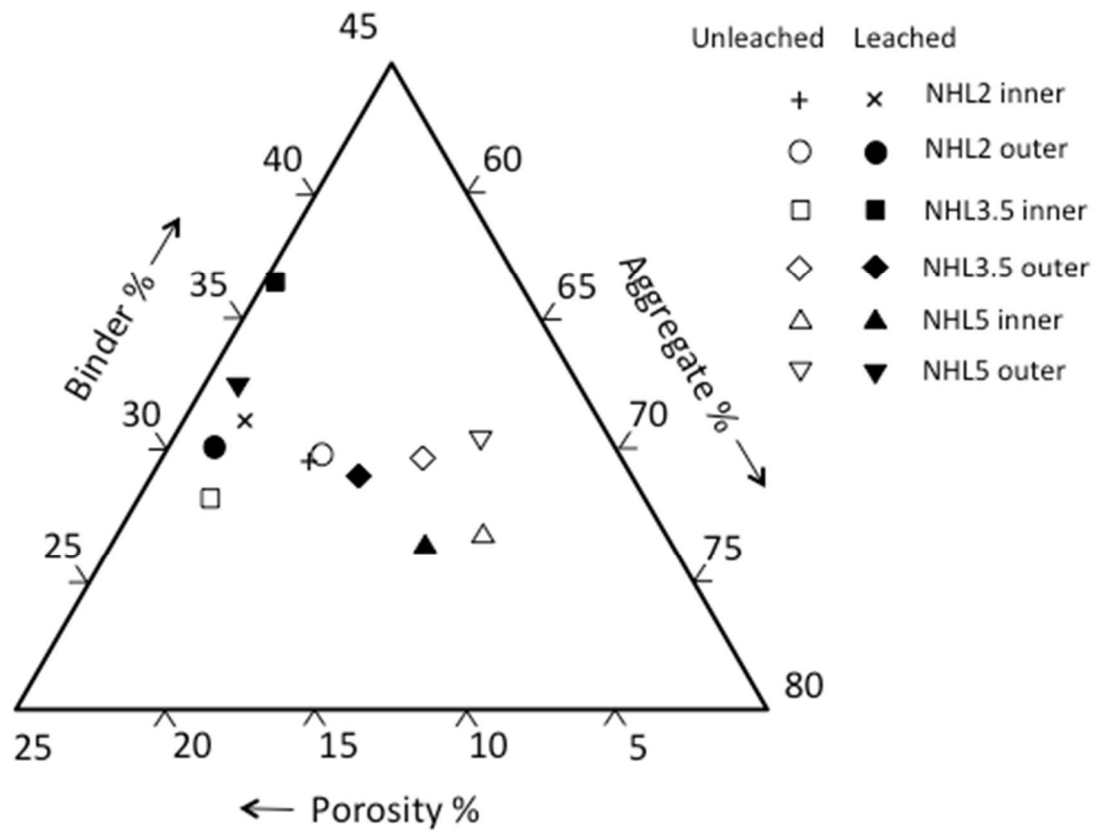


Figure 6: Thin section point counting data for carbonated mortars showing the effect of leaching in ammonium nitrate for 36 days

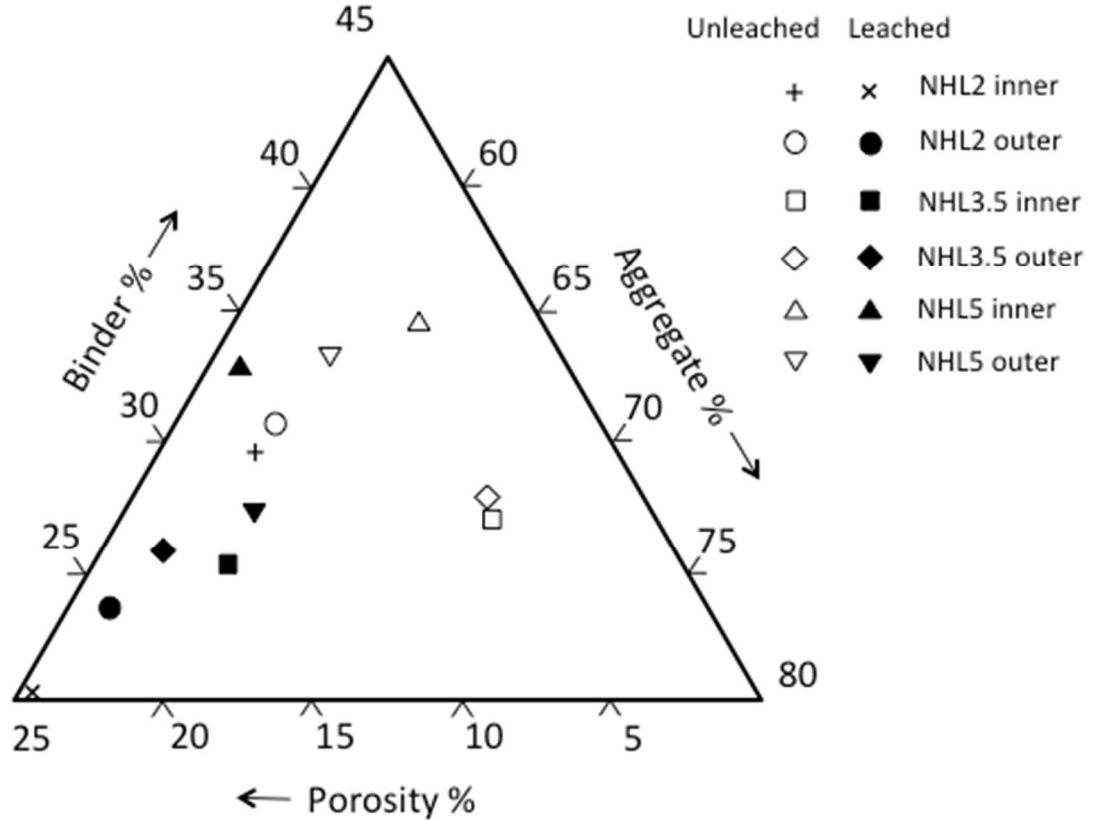


Figure 7: Thin section point counting data for uncarbonated mortars showing the effect of leaching in ammonium nitrate for 36 days

Recognising that there is a 4% experimental error on the points in Figures 6 and 7 [10], the differences in composition between unleached and leached specimens are within experimental error for four out of the six carbonated mortars, whilst the differences for all the uncarbonated mortars are both significantly larger than experimental error and tend to align with the vector predicted from Figure 5. Even so, the small differences for the carbonated mortars (Figure 6) also tend to align with the predicted vector. The thin section for the NHL3.5 inner zone shows the reverse of the predicted vector: a lower porosity/higher binder content in the leached than in the unleached specimen. This is not consistent with the image shown in Figure 3D, which is of a different thin section taken from the same zone and shows much higher and coarser porosity. This suggests incomplete mixing and points to a possible reason for the observed anomalous leaching resistance of carbonated NHL3.5 mortar, discussed further below.

5 DISCUSSION

All the results presented here relate to carbonated natural hydraulic lime mortars: they can be taken as being relevant to mortar near the surface of masonry constructions, which has had the opportunity during its lifetime to dry sufficiently to allow carbonation to occur, i.e. it has not been continuously saturated, even though moisture may be present now or in the future to facilitate binder leaching. Strength measurements have established that ammonium nitrate successfully accelerates the leaching of binder from carbonated mortars, just as for uncarbonated mortars [10]. However, the reductions in strength are less marked than for uncarbonated mortars: whereas uncarbonated mortars lost 96-99.5% of their compressive strength over 169 days [10], the carbonated mortars lost 73-91% over the same period. Sorptivity of carbonated mortar is affected by leaching, and this agrees with the broad trend in porosity shown by the point counting analysis. This is also less severe than in the uncarbonated mortars [10], for which sorptivity increased by between 30 and 150%. These results suggest that carbonated mortars are more resistant to leaching than uncarbonated mortars, and this is in line with the relative solubilities of CaCO_3 and Ca(OH)_2 , the predominant binder material in the respective mortars. Additionally, whereas in uncarbonated mortars the resistance to leaching is strongly influenced by the relative proportion of C-S-H within the matrix, with the most hydraulic lime (NHL5) showing the highest resistance, in carbonated mortars this effect is less dramatic as the lowering of binder solubility that comes with carbonation mitigates the influence of hydraulicity.

In part 1 [10] the leaching rate of uncarbonated mortars was quantified by the size of the alkaline zone visible in the fracture surface, when sprayed with phenolphthalein. This approach is not possible in these fully carbonated mortars because, by definition, there is no alkaline zone visible. Therefore another approach based on the decrease of strength will be adopted. The data presented in Table 3 above and in Table 3 of part 1 [10] suggest that the compressive strength decreases exponentially with time of leaching according to a relationship of the form:

$$f_{cu}(t) / f_{cu}(0) = e^{-bt} \quad (3)$$

where $f_{cu}(t)$ is the strength after leaching for time t and $f_{cu}(0)$ is the strength before leaching. A graph of $\ln(f_{cu}(t) / f_{cu}(0))$ against t should give a straight line of slope $-b$ and b is therefore a first order rate constant for the strength reduction process. Combining data for uncarbonated mortars from Table 3 of part 1 [10] and for carbonated mortars from Table 3 above, Figure 8 confirms that the logarithm of the strength, relative to that of the untreated specimens, decreases linearly with time, giving the values of b summarised in Table 4. For clarity, the regression lines are omitted from Figure 8 but it can be noted

from Table 4 that, in four of the six sets of data, the value of R^2 (four points in each graph) is high. The value of b is consistently larger for uncarbonated than carbonated mortars made with all limes, and decreases in the order $NHL2 > NHL5$, reflecting the more rapid strength reductions in uncarbonated mortars and those of less hydraulic binders. However, the uncarbonated NHL3.5 mortars appear to be more resistant than both NHL2 and NHL5, whereas the carbonated NHL3.5 mortars are equally resistant to the NHL2 and less resistant than NHL5.

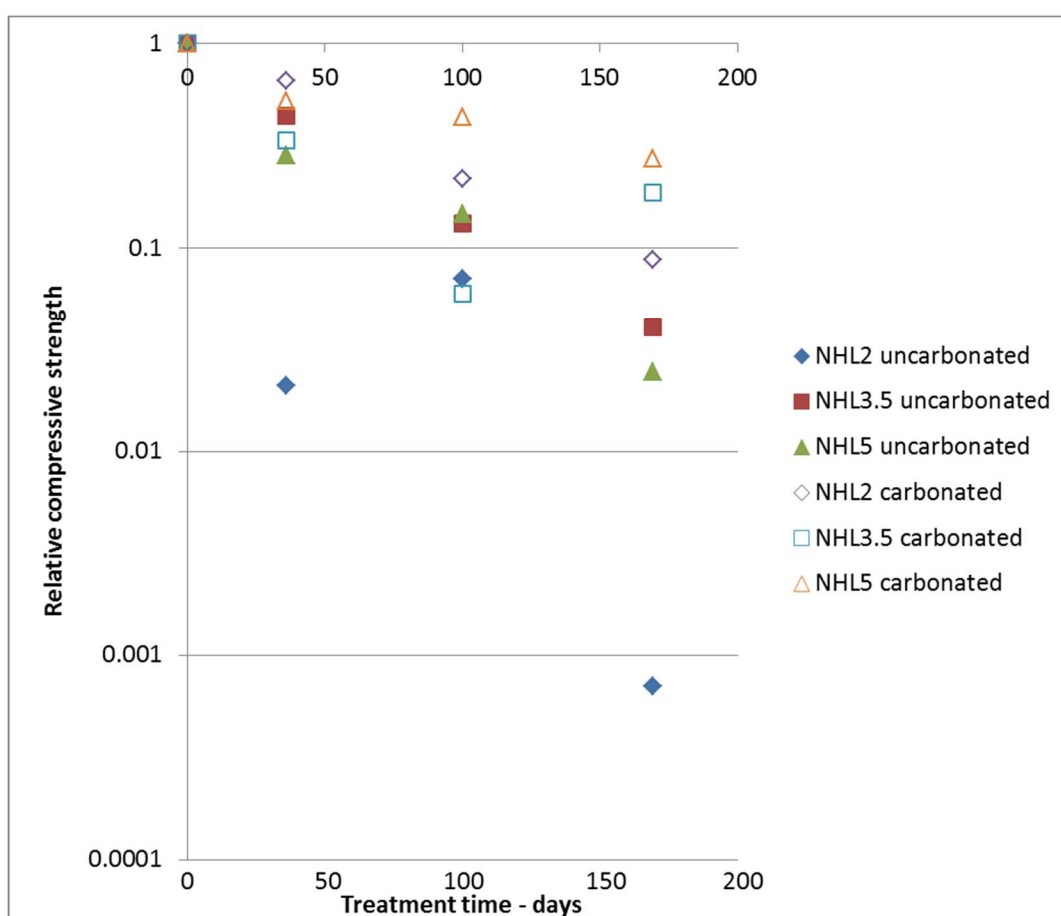


Figure 8: Strength reduction in uncarbonated and carbonated NHL mortars leached in ammonium nitrate

Table 4: Strength reduction kinetics in NHL mortars treated with 1M NH₄NO₃.

	NHL2 uncarbonated	NHL3.5 uncarbonated	NHL5 uncarbonated	NHL2 carbonated	NHL3.5 carbonated	NHL5 carbonated
Rate constant, b (day ⁻¹)	0.041	0.019	0.022	0.015	0.015	0.008
R ²	0.71	0.995	0.96	0.996	0.33	0.85
Estimated time to 20mm leached depth (days)	34	73	63	92	92	173
k (equation 5) (mm/day ^{1/2})	3.43	2.34	2.51	2.09	2.09	1.52
Leaching resistance (1/k)	0.29	0.43	0.40	0.48	0.48	0.66

Now, figure 12 of part 1 [10] shows that a leached depth of 20mm is achieved in uncarbonated specimens in 42 days for NHL2, 50 days for NHL3.5 and 73 days for NHL5 mortars. The kinetic parameters in Table 4 show that these times correspond to residual strengths ($f_{cu}(t) / f_{cu}(0)$) of 0.18, 0.39 and 0.20 respectively, giving a mean value of 0.25 (i.e. residual strength is 25% of untreated strength). Assuming that the same relationship between strength and leached depth applies to carbonated mortar, where CaCO₃ is leached (equation 2), and to uncarbonated mortar, where Ca(OH)₂ is leached (equation 1), then the time to a residual strength of 25% gives an estimate of the time to a 20mm leached depth. These estimated times are also shown in table 4. Finally, part 1 [10] developed a relationship between leached depth h and treatment time t (equation 5), where k is a constant, the reciprocal of which is an index of resistance to leaching (which is also shown in table 4):

$$h = kt^{1/2} \quad (5)$$

Table 4 shows that the time to a leached depth of 20mm in uncarbonated specimens as estimated by this procedure is slightly different from that directly measured by phenolphthalein spraying, given in figure 12 of part 1 [10]. However, for the sake of consistency in the analysis of the different materials, the values from Table 4 will be adopted here. Leaving aside the data for the NHL3.5 mortars, the index of resistance to leaching ($1/k$) is 38% higher for NHL5 mortar than for NHL2, whether uncarbonated or carbonated, and is 65% higher in carbonated than in uncarbonated mortar, whether NHL2 or NHL5. This is in agreement with the explanation, offered previously, that the more hydraulic lime is more resistant to leaching and that conversion of the Ca(OH)₂ to CaCO₃ by carbonation makes the mortar more resistant to leaching. It is particularly striking that the percentage increases in the index of resistance agree so closely. It may be noted that the square root dependence in equation 5 means that a 1.65-fold increase in the index of resistance as a result of carbonation increases the time to a given depth of leaching by a factor of 2.75.

Considering the results for NHL3.5 and the position of this binder in the sequence, the regression line for the strength decay of carbonated mortars (Figure 8) has an R^2 value of 0.33. This is not statistically significant and this implies a wide confidence interval on the value of b and hence on the estimated leaching resistance. This is probably related to the anomalous results of the thin section analysis (Figures 3D and 6) discussed above. If the NHL3.5 mortars were incompletely mixed or compacted a wider scatter in the strength results would be expected, particularly as each point in Figure 8 is from a single specimen. A poorly compacted specimen would have low strength and if this were the single carbonated NHL3.5 specimen in Figure 8 which shows much lower relative strength after 100 days leaching it would have a substantial effect on the slope of the strength reduction regression line. This suggests that the true regression for NHL3.5 might lie between those for NHL5 (smaller strength reduction) and NHL2 (larger strength reduction), but this cannot be confirmed without repeating the experiment. Thus the data are not inconsistent with placing carbonated NHL3.5 mortars in order of leaching resistance between NHL2 and NHL5 mortars. Also, in uncarbonated mortars the values estimated from the strength decay are different from those obtained by direct observation of the carbonation front (figure 12 of part 1[10]): the latter place uncarbonated NHL3.5 between NHL2 and NHL5 mortars. Thus, again there is evidence in support of a trend of increasing leaching resistance in the order $\text{NHL2} < \text{NHL3.5} < \text{NHL5}$. Therefore, it seems safe to say that high confidence can be ascribed to the values of leaching resistance of NHL2 and NHL5 mortars, but those of NHL3.5 have low confidence even though it is likely that the latter binder fits in the sequence between the other two.

All this has clear implications for the performance of NHL mortars subject to long term saturated conditions: higher hydraulicity binders perform better and carbonated mortars perform better than uncarbonated mortars. Based on the results presented here and in part 1 [10] the index of resistance to leaching, combined with the acceleration factor of 20 for the ammonium nitrate leachant established in [10], enables estimates to be made of the time to a certain depth of leaching by water and of the depth after a certain time of leaching. These estimates are of practical importance in field performance of lime mortars and some examples are given in Table 5. Table 5 shows the depth of leaching after exposure to water for one and 100 years, and the time taken to leach to a depth of 20mm (taken as equivalent to a residual compressive strength of 25% - Table 4) and 50mm (taken as half the depth of a typical mortar joint in the external face of a wall).

Table 5: Estimated leaching in NHL mortars exposed to water.

	NHL2 uncarbonated	NHL3.5 uncarbonated	NHL5 uncarbonated	NHL2 carbonated	NHL3.5 carbonated	NHL5 carbonated
Leached depth after one year (mm)	3.5	2	2.5	2	2	1.5
Leached depth after 100 years (mm)	33	22	24	20	20	15
Time to leach to 20mm deep (years)	40	80	70	100	100	190
Time to leach to 50mm deep (years)	230	500	440	630	630	1200

Reduction in mortar strength is not a serious structural problem in service because the compressive strength of a wall is dominated by the strength of the unit rather than the mortar. For example, structural design codes suggest that even when the mortar used with a given unit has a strength of only 1.5 MPa instead of 16MPa the wall strength is reduced by only 50%, not the anticipated 90% [23]. However, using strength reduction as a proxy for loss of durability, dimensional stability, cohesion and adhesion of the mortar, all relationships that are well established for cementitious materials [24], it is clear that binder leaching will lead to erosion of the mortar bed and ultimately to loss of units from the masonry. The data in Table 4 confirm that any measures that will enhance the degree of carbonation of mortar will significantly prolong the service life of masonry.

The results from this work are generally consistent with the differences in solubility of Ca(OH)_2 and CaCO_3 but some points of detail will be explored next. The composition of the NHL2 binder [10] and the mortars (Table 1) suggest that the highest proportion of calcium in the hardened mortars tested is 42g Ca/kg or 73.5kg Ca/m³ (the more hydraulic binders have lesser amounts of soluble Ca). In the accelerated leaching experiment 20 specimens (9kg of mortar) were exposed to 15L of leachant to produce $\text{Ca(NO}_3)_2$, whose solubility is 1440g/L (351g Ca/L). Even if all the Ca present in the mortar specimens were leached into solution by the end of the experiment this would deliver only 25.2g Ca/L (7% of the saturation solubility level). This confirms that the experimental conditions have NH_4NO_3 in excess and that laboratory leaching is not solubility-limited. However, field leaching by water is a different matter. The solubility of Ca(OH)_2 is 1.6g/L (0.86g Ca/L) and of CaCO_3 is 0.0066g/L (0.00264g Ca/L). Thus 1kg of mortar requires 26L of water to dissolve the Ca if the latter were present as Ca(OH)_2 and 6363L of water if it were CaCO_3 . Thus static leaching is clearly solubility-limited because it is improbable that mortar will be constantly surrounded by so much water. However, a different picture is presented by considering rainfall on unprotected masonry. This will pass through a

10mm thick bed joint, estimated to contain 17.5kg mortar per m². 17.5kg of mortar contains 735g Ca, which, if present as Ca(OH)₂, will dissolve in 854L of water. Taking Scotland's rainfall as 1500mm/year [25], corresponding to 1500L/m² surface area, this could take less than a year. Likewise, if the mortar were carbonated the CaCO₃ would require 185 years of rainfall. Because water from rain flows unevenly over surfaces and can be concentrated into particular areas, these figures may well be conservative. At the other extreme of climate related water flow, Hall et al [4] calculated the upward water flow as a result of evaporative pumping in the London and Athens climates. For a 300mm thick wall (with no damp course) with evaporation from both sides the annual water flow through the bed joint in a wall in London is 1380L/m² and in Athens is 2633L/m². These figures suggest that uncarbonated mortar is vulnerable to complete binder loss in less than one year and that even carbonated mortar in the Athens climate may be fully leached in 100 years. These calculations suggest that it is reasonable to use accelerated leaching experiments, where the leachant solution is in excess compared to the amount of Ca in the mortar, to indicate the scale of the binder leaching problem in field situations, where water is flowing at such a rate as to be also in excess. Stationary water is expected to be less of a problem.

Whereas the results presented here are a step towards a prediction model, further investigations are needed in order to establish the effects of variables such as water composition (e.g. Hardness and pH) and to study possible differences between 'site-leached' and 'accelerated-leached' mortars.

6 CONCLUSIONS

1. Molar ammonium nitrate solution has been shown to be a satisfactory leachant for accelerated deterioration studies on natural hydraulic lime binders in masonry mortar. It is able to extract calcium from laboratory specimens in a reasonable time for comparative studies of binder loss in carbonated mortar.
2. Leaching of calcium from the carbonated binder reduces the strength and increases the sorptivity of NHL mortar, with the kinetics following a first-order process. The rate constant increases from NHL5 to NHL3.5 to NHL2, i.e. as the lime binder becomes less hydraulic. This is consistent with carbonated NHL5 mortars having the highest leaching resistance.

3. The resistance to leaching of a given carbonated binder is higher than that of the same binder when uncarbonated. The experimental evidence suggests the following composite order of increasing resistance to leaching: uncarbonated NHL2 < uncarbonated NHL3.5 \approx uncarbonated NHL5 \approx carbonated NHL2 \approx carbonated NHL3.5 < carbonated NHL5.

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